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(54) PROCESS FOR PRODUCING BONDED COMPOSITE.

(57) Bonded composites comprising a hardened silicone and various solid materials can be produced with ease, sureness, and high accuracy without any previous primer treatment, by keeping an addition reaction-hardenable silicone containing 0.05 to 20 wt% of a silicon atombound, hydrolyzable group in contact with a solid material at temperatures not lower than room temperature. This process is applicable to wide fields including machines, electrics, electronics, buildings, and aircrafts, since it does not cause environmental pollution.

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SPECIFICATION

PROCESS FOR PRODUCING A BONDED COMPOSITE

Technical Field:

The present invention relates to a process for producing a bonded composite. More particularly, the invention relates to a process for producing a bonded composite of a specified cured product of addition reaction-curable silicone and a solid substance.

Background Art:

Generally, an organopolysiloxane composition which is cured through an addition reaction between a lower alkenyl group bonded to a silicon atom and a hydrogen atom bonded to a silicon atom has only poor adhesion to other materials. To bond such an organopolysiloxane composition to another material, the surface of the material must be treated with a primer before it is contacted with the organopolysiloxane composition, and the composition is cured after the contact to bond them together in the prior art. However, the treatment with the primer invites various disadvantages. Recently, there has been proposed an organopolysiloxane composition curable through an addition reaction between a lower alkenyl group bonded to a silicon atom and

a hydrogen atom bonded to a silicon atom, which composition exhibits an excellent adhesion without any previous treatment of the surface of an adherend with a primer as disclosed in the specifications of  
5 Japanese Patent Publications Nos 48146/1977, 9183/1981 and 5836/1981. Such an addition reaction-curable organopolysiloxane composition is generally a one-component or two-component liquid which cures and adheres at room temperature or by relatively  
10 slight heating. Therefore, said composition is usable as a coating material, casting material, impregnating material or adhesive and bonded composites of various shapes have been obtained.

However, because said composition is liquid,  
15 it is difficult in practice to coat only a specified, small part and it often exerts unfavorable influences on the surroundings. For example, the fluid composition spreads over a part which is not to be coated or which should not be coated. Further, a  
20 low-molecular organopolysiloxane in the composition is scattered into the surroundings to stain the latter in the step of curing by heating and, therefore, problems such as a reduction in insulating power or poor adhesion to another material are  
25 posed. Examples of processes which have been

employed to prevent such staining include a process wherein the amount of the composition to be applied and the application area are controlled precisely,  
5      a process wherein parts other than the surface to be coated are masked with a masking tape, a process wherein a dam is provided for preventing superfluous spread and a process wherein the low molecular weight organopolysiloxane is washed away with a solvent or a gas or the unnecessary silicone is removed by decomposition after the curing of the  
10     composition. However, these conventional processes are disadvantageous in that expensive precision apparatuses are required, complicated steps are necessitated, the coated surface is damaged by the  
15     after-treatment and some adherends have a shape or structure which cannot be easily protected from the staining.

An object of the present invention is to provide a process for producing a firmly bonded composite comprising a cured product of an addition reaction-curable silicone and a solid substance wherein only that part of the surface of the solid substance which is to be coated with the cured product can be coated and the surroundings are not stained with  
20     a low molecular weight organopolysiloxane.  
25

Disclosure of Invention:

The object of the present invention is attained by keeping the cured product of addition reaction-curable silicone containing 0.05 to 20 wt.% of a silicon atom-bonded hydrolyzable group in contact with a solid substance at room temperature or a higher temperature.

Best Mode for Carrying Out the Invention:

The term "cured product of addition reaction-curable silicone" used herein refers to a cured silicone obtained by an addition reaction between an alkenyl group bonded to a silicon atom and a hydrogen atom bonded to a silicon atom.

A typical example of the cured product of addition reaction-curable silicone is a product obtained by leaving a composition to stand at room temperature or by heating the composition to cure the same, which composition comprises (a) an organopolysiloxane containing at least two silicon atom-bonded alkenyl groups in the molecule, (b) an organopolysiloxane containing at least two silicon atom-bonded hydrogen atoms in the molecule (with the proviso that the average of the total number of the silicon atom-bonded alkenyl groups in the molecule of the component (a) and the silicon

atom-bonded hydrogen atoms in the molecule of the component (b) is at least 4.1) and (c) a platinum catalyst. Other examples of the cured products are the same one as above except that the organo-polysiloxane used as the component (a) or (b) is replaced with an organosilane and the same one as above except that the platinum catalyst used as the component (c) is replaced with another addition reaction catalyst.

The silicon atom-bonded hydrolyzable group contained in an amount of 0.05 to 20 wt.% in the cured product of addition reaction-curable silicone may be that of an organosilicon compound contained in its free form in said cured product or that of a polysiloxane constituting said cured product.

Irrespectively of the type, the amount of the silicon atom-bonded hydrolyzable groups in the cured product of the addition reaction-curable silicone is 0.05 to 20 wt.%, preferably 0.1 to 10 wt.% based on the cured product, because when this amount is smaller than 0.05 wt.%, no sufficient adhesive power can be obtained and when it exceeds 20 wt.%, the effects are no more improved. The cured product of addition reaction-curable silicone in which the silicon atom-bonded hydrolyzable group

is contained in the organosilicon compound in free form contained in said cured silicone product (type A) is obtained by leaving a composition to stand at room temperature or by heating it, which 5 composition comprises the above mentioned components (a), (b), (c) and an organosilicon compound (d) having at least one silicon atom-bonded hydrolyzable group in the molecule but free from any silicon atom-bonded alkenyl group or silicon atom-bonded 10 hydrogen atom. Alternatively, it is obtained by curing the composition comprising the above-mentioned components (a), (b) and (c) by leaving it to stand at room temperature or by heating it and then applying an organosilicon compound (e) 15 having at least one silicon atom-bonded hydrolyzable group in the molecule thereto or impregnating the former with the latter.

The organopolysiloxane having at least two silicon atom-bonded alkenyl groups in the molecule 20 of component (a) constituting the cured product of the addition reaction-curable silicone of type A is subjected to an addition reaction with the component (b) by a catalytic effect of the component (c) to form a cross-linked product in the form of a 25 gel-like, rubbery or rigid resin-like.

5

The molecular shape may be any of linear, branched linear, cyclic, reticulate and three-dimensional shapes. The polymer may be either a homopolymer or a copolymer. As for the degree of the polymerization, the products range from an oligomer to a high polymer including a 10,000-mer. The product is preferably in liquid form or raw rubber-like form at room temperature.

10

15

The alkenyl groups include, for example, vinyl, allyl, 1-propenyl and isopropenyl groups, among which a vinyl group is preferred. At least two alkenyl groups must be present in the molecule of the organopolysiloxane. The positions of the alkenyl groups are not particularly limited, though it is preferred that they are positioned apart from each other as far as possible. For example, the alkenyl groups are positioned preferably at both ends of the organopolysiloxane.

20

Other organic groups include, for example, methyl, ethyl, n-propyl, octyl, cyclohexyl, phenyl and 3,3,3-trifluoropropyl groups.

25

At least 50 molar % of the organic groups other than the alkenyl groups comprise methyl groups. When a phenyl group is present, its amount is preferably up to 30 molar % based on the total

organic groups and the maximum is 10 molar %. A small amount of the silicon atom-bonded hydroxyl group may also be present.

The organopolysiloxane having at least two silicon atom-bonded hydrogen atoms in the molecule of component (b) constituting the cured product of the addition reaction-curable silicone of type A is subjected to an addition reaction with the component (a) by a catalytic effect of the component (c) to form a cross-linked product in the form of a gel-like, rubbery or rigid product-like. The molecular shape may be any of linear, branched linear, cyclic, reticulate and three-dimensional shapes. The polymer may be either a homopolymer or a copolymer. As for the degree of the polymerization, the products range from a dimer to a high polymer including a 5,000-mer. At least two silicon atom-bonded hydrogen atoms should be present in the molecule of the organopolysiloxane. The positions of the hydrogen atoms are not particularly limited. However, it is preferred that they are positioned apart from each other as far as possible. A reason why the total number of the silicon atom-bonded lower alkenyl groups in the molecule of the component (a) and the silicon atom-bonded hydrogen

atoms in the molecule of the component (b) is controlled to at least 4.1 on average is that the state of the resulting, cured product is excellent under such a condition. The organic groups 5 include, for example, methyl, ethyl, n-propyl, octyl, cyclohexyl, phenyl, tolyl, 3,3,3-trifluoro-propyl, benzyl, p-chlorophenyl and cyanoethyl groups.

Preferably, at least 50 molar % of the organic 10 groups comprise methyl groups.

To realize a suitable, cured state, it is preferred to use the component (b) in an amount (parts by weight) satisfying the following equation:

15            $\frac{[\text{Equivalent of the silicon atom-bonded hydrogen atoms in component (b)}]}{[\text{equivalent of the silicon atom-bonded lower alkenyl groups in the component (a)}]} = 0.3/1 \text{ to } 6/1$

for 100 parts by weight of the component (a)

20           The component (c) is a catalyst for the addition reaction between the silicon atom-bonded lower alkenyl group in the component (a) and the silicon atom-bonded hydrogen atom in the component (b). The components (c) include, for example, 25 finely pulverized platinum element, finely

pulverized platinum dispersed on a carbon powder,  
platinum black, chloroplatinic acid, a complex  
salt of platinum with an olefin, platinum bis(acetyl-  
acetone), tetrakis(triphenylphosphine)palladium,  
5 a mixture of palladium black and triphenylphosphine  
and a rhodium catalyst. The component (c) is used  
in a so-called catalytic amount. When the component  
(c) is a platinum compound, it is used preferably  
in an amount of 0.1 to 100 parts by weight (in  
10 terms of platinum) for million parts by weight of  
the cured silicone product.

The organosilicon compound (d) containing at  
least one silicon atom-bonded hydrolyzable group  
in the molecule but free of the silicon atom-bonded  
15 alkenyl group or silicon atom-bonded hydrogen atom  
is used for making the cured silicone product  
adherent to the solid substance. The silicon atom-  
bonded hydrolyzable groups include, for example,  
alkoxy groups such as methoxy, ethoxy, n-propoxy  
20 and methoxyethoxy groups; acyloxy groups such as  
acetoxy, propionoxy and 2-ethylhexanoxy groups;  
N-organoamido groups such as N-methylacetamido,  
N-ethylacetamido and N-methylpropioamide groups;  
ketoxime groups such as methyl ethyl ketoxime and  
25 diethyl ketoxime groups; and alkenyloxy groups

such as isopropenyloxy, 1-phenyl-1-ethenyloxy and isobutenyloxy groups.

From the viewpoint of the adhesion improvement, it is preferred that at least 3 silicon atom-bonded hydrolyzable groups are present in a molecule.

From the same viewpoint as above, preferred hydrolyzable groups are alkoxy groups such as methoxy and ethoxy groups; acyloxy groups such as acetoxy group; and ketoxime groups such as methyl ethyl ketoxime group.

The component (d) may contain, in addition to the hydrolyzable group, an organic group such as an alkyl, aryl, halogenated alkyl, acryloxyalkyl, methacryloxyalkyl or glycidyloxyalkyl group. The organosilicon compounds (d) include, for example, silane and polysiloxanes. The polysiloxane may be a polymer of at least two monomeric units. The molecular shape of the component (d) may be any of linear, branched linear, cyclic, reticulate and three-dimensional shapes. The component (d) is preferably a silane or a polysiloxane having a low degree of polymerization.

The organosilicon compounds include, for example, methyltriethoxysilane, n-propyltri(methoxyethoxy)silane, phenyltrimethoxysilane, methylphenyl-

dimethoxysilane,  $\gamma$ -methacryloxypropyltrimethoxy-  
silane,  $\gamma$ -glycidyloxypropyltriethoxysilane,  
3,3,3-trifluoropropyltriethoxysilane and partial  
hydrolyzates of these silanes; (methoxyethoxy)  
5      o-silicate; dimethylpolysiloxane of a low degree  
of polymerization both ends of which are blocked  
with methyldiethoxysilyl groups; and compounds  
obtained by replacing part or the whole of the  
alkoxy groups of the above-mentioned organosilicon  
10     compounds with acetoxy, methyl ethyl ketoxime,  
N-methylacetamido or isopropenyoxy group.

The organosilicon compound (e) having at least  
one silicon atom-bonded hydrolyzable group in the  
molecule has the same effects as those of the com-  
15     ponent (d). The compounds (e) include those listed  
above with reference to the component (d) and, in  
addition, organosilicon compounds containing a  
silicon atom-bonded alkenyl group or a silicon  
atom-bonded hydrogen atom.

20     The silicon atom-bonded alkenyl groups include  
those listed above with reference to the component  
(a).

25     The components (e) include, in addition to  
those listed above with reference to the component  
(d), vinyltrimethoxysilane, allyltriethoxysilane,

methylvinyldiethoxysilane, vinyltri(methoxyethoxy)-silane, partial hydrolyzates of these silanes, dimethylpolysiloxane having a low degree of polymerization and terminated with vinyldimethoxysilyl groups at both ends, and compounds obtained by replacing part or the whole alkoxy groups of the above-mentioned organosilicon compounds with acetoxy, methyl ethyl ketoxime, N-methylacetamido or isopropenyloxy group.

The component (d) is used in such an amount that 0.05 to 20 wt.% of the silicon atom-bonded hydrolyzable groups would be contained in the cured product of addition reaction-curable silicone.

The component (e) is applied to the cured product of the addition reaction-curable silicone comprising the components (a) to (c) by coating or impregnation and, therefore, it is not distributed uniformly but present only locally in many cases.

The component (e) is used in such an amount that the silicon atom-bonded hydrolyzable group would be contained in an amount of 0.05 to 20 wt.% on an average in said cured product.

The cured product of addition reaction-curable silicone in which the silicon atom-bonded hydrolyzable group is contained in the polysiloxane

constituting the cured product (type B) is obtained by a process wherein a composition comprising the above-mentioned components (a) to (c) and an organosilicon compound (f) having at least one silicon atom-bonded hydrolyzable group and at least one silicon atom-bonded alkenyl group or silicon atom-bonded hydrogen atom in the molecule is left to stand at room temperature or heated to cure the composition, a process wherein a composition comprising an organopolysiloxane (a') having at least two silicon atom-bonded alkenyl groups and at least one silicon atom-bonded hydrolyzable group in the molecule, an organopolysiloxane (b) having at least two silicon atom-bonded hydrogen atoms in the molecule and the component (c) is left to stand at room temperature or heated to cure the same, a process wherein a composition comprising an organopolysiloxane (a) having at least two silicon atom-bonded alkenyl groups in the molecule, an organopolysiloxane (b') having at least two silicon atom-bonded hydrogen atoms and at least one silicon atom-bonded hydrolyzable group in the molecule and the component (c) is left to stand at room temperature or heated to cure the same or a process wherein a composition comprising the components

(a'), (b') and (c) is left to stand at room temperature or heated to cure the same.

The component (a') is essentially the same as the component (a) except that the former has at least one silicon atom-bonded hydrolyzable group in the molecule. The above-mentioned details of the component (a) may be applied also to the component (a').

The component (b') is essentially the same as the component (b) except that the former has at least one silicon atom-bonded hydrolyzable group in the molecule. The above-mentioned details of the component (b) may be applied also to the component (b').

It is preferred that both components (a') and (b') have at least three silicon atom-bonded hydrolyzable groups in the respective molecules. The hydrolyzable groups are similar to those listed above with reference to the component (d).

Each of the components constituting the cured product of the addition reaction-curable silicone may be either alone or in the form of a mixture of two or more compounds. The composition may contain, in addition to the above-mentioned indispensable components, a filler or a pigment such as fumed

silica, precipitated silica, fine quartz powder,  
diatomaceous earth, talc, aluminum silicate,  
zirconium silicate, alumina, calcium carbonate,  
zinc oxide, titanium dioxide, ferric oxide or glass  
fibers; an addition reaction retardant such as  
benzotriazole, dimethyl sulfoxide or an alkyne  
alcohol; a flame retardancy-improver such as carbon  
black, fumed titanium dioxide or manganese carbonate;  
a heat stabilizer such as cerium oxide; a pigment  
other than those listed above; and an organic  
solvent.

The composition comprising the above-mentioned  
indispensable components and the additional com-  
ponents used if necessary is cured by leaving them  
to stand at room temperature or under heating.  
Thus, the cured product is obtained which is in  
the form of a gel-like, rubbery or rigid resin  
depending on varieties of the components and the  
proportion of them. To obtain the cured product  
of the addition reaction-curable silicone having  
an excellent adhesion, it is preferred to cure the  
silicone to obtain a rubbery product having a  
hardness of up to 20 as determined by means of a  
hardness tester according to a specification of JIS  
K 6301, to cure the silicone at a temperature of

room temperature to 200°C in a moisture-free atmosphere such as dry air or dry nitrogen in a short time or to cure the silicone at room temperature to 200°C in a closed vessel in a short time.

- 5       The composition comprising the indispensable components and, if necessary, the additional components is cured generally while it is in contact with another material. The curing may be effected by, for example, a process wherein the composition  
10      is cured on a material having an excellent releasing property or a material having substantially no releasing property in an open system, a process wherein the composition is cured in a mold having an excellent releasing property in an open system,  
15      a process wherein the composition interposed between materials having an excellent releasing property is cured, a process wherein the composition interposed between a material having an excellent releasing property and a material having  
20      substantially no releasing property is cured, a process wherein the composition is cured in a mold having an excellent releasing property and sealed with a material having an excellent releasing property.  
25      The starting materials used for preparing the

materials or molds having an excellent releasing property or substantially no releasing property include, for example, fluororesins such as tetrafluoroethylene resin and vinylidene fluoride resin, polyethylene resin, polypropylene resin, methacrylic resin, polycarbonate resin, stainless steel and acetylcellulose. These materials may be in the form of, for example, sheets, films, woven fabrics and plates.

The starting materials used for preparing the materials or molds having substantially no releasing property include, for example, plastics such as polyimide resin, polyester resin; epoxy resin, urethane resin and polyphenylene resin; iron, nickel, copper, aluminum, zinc, chromium, cobalt and alloys of these metals as well as these metals having an oxide film on the surface thereof; glass and ceramics; and woods and papers. These materials may be in the form of, for example, sheets, films, woven fabrics and plates.

The other material having an excellent releasing property is peeled off from the resulting cured product, if necessary. Alternatively, the resulting cured product is taken out of the mold.

The cured product of the addition reaction-curable

silicone or the laminate thereof with another material is used as it is or after cutting or punching the same to obtain pieces having a suitable shape and size. The cured silicone part of the 5 product is adhered to a specified part or the whole surface of a solid substance or, alternatively, it is interposed between two solid substances. They are maintained at a temperature of at least room temperature, preferably 40 to 200°C under pressure 10 to obtain a bonded composite comprising the cured product of the addition reaction-cured silicone or a bonded composite comprising the laminate of the cured product and the other material firmly bonded with the solid substance in one body. The time 15 preferred for realizing the firm adhesion is at least one hour at 50°C, at least 10 min at 100°C and at least 5 min at 200°C.

The solid substances include those having a given shape made of metals such as iron, titanium, 20 nickel, copper, aluminum, zinc, tin, chromium, or cobalt, alloys of them and these metals having an oxide film on the surface thereof; glasses; stones; ceramics such as earthenware, porcelain and new ceramics; silicon and germanium; plastics such as 25 epoxy, polyester, unsaturated polyester, polyamide,

polyimide, urethane, melamine, acrylic, urea,  
silicone, polyphenylene oxide and polyphenylene  
sulfide resins; rubbers; woods; and papers. They  
may be used either alone or in the form of a com-  
5 posite material of them. The shape of them may  
be any of sheets, films, woven fabrics, plates,  
filaments, rods, tubes, spheres, boxes and cubes.  
The solid substance may be a single substance or  
a part of machines, devices, jigs, electric appli-  
10 ances, electronic appliances, electric parts,  
electronic parts, automobiles, aircrafts, rockets,  
vehicles, ships, communication apparatuses, measur-  
ing instruments, cables, robots, facilities and  
buildings.

15 According to the present invention, the  
following effects can be obtained:

- (1) The cured silicone product can be bonded  
to the solid substance without using any liquid,  
curable adhesive to be interposed between them.
- 20 (2) Only that part which is to be coated with  
the cured silicone substance by adhesion can be  
coated accurately and easily.
- (3) Since the cured silicone product is used,  
the surroundings of the coated part are not  
25 stained by an organopolysiloxane having a low

degree of polymerization.

(4) Since the cured silicone product is used, even a perpendicular or suspended part can be coated if it is fixed with an adhesive tape or  
5 the like.

In the bonded composite prepared by the process of the present invention, only that part which is to be coated is coated with the cured product of the addition reaction-curable silicone or with a  
10 laminate of the cured product and another material and the surroundings are not stained. Thus, the present invention realizes an improved capacity and the uses of the product are further broadened.

15 The following examples will further illustrate the present invention. In the examples, parts and percentages are given by weight and the viscosities are those determined at 25°C unless otherwise stated.

Example 1

20 97 parts of dimethylpolysiloxane (a) having dimethylvinylsilyl groups at both ends and a viscosity of 2000 CS was mixed thoroughly with 2 parts of methylhydrogenpolysiloxane (b) having trimethylsilyl groups at both ends and a viscosity  
25 of 10 CS, 3 parts of vinyltrimethoxysilane (f) and

5 ppm (in terms of platinum), based on the total amount, of a solution of chloroplatinic acid in ethanol. The value of [equivalents of silicon atom-bonded hydrogen atoms in component (b)] / [equivalents of silicon atom-bonded vinyl groups in component (a)] was 2.5/1. The mixture was poured into a tetrafluoroethylene resin mold to a thickness of 7 mm and then cured to form a rubbery product by leaving it to stand in dry air in an oven of open system at 100°C for 5 min. The product was taken out of the oven and left to cool to room temperature. The cured silicone rubber was taken out of the mold and its hardness was measured with a hardness meter for rubber according to the specification of JIS K 6301. The hardness was 5.

The cured silicone rubber was closely contacted with a surface of a flat glass and left to stand in an oven at 100°C for 30 min to obtain a bonded composite comprising the cured silicone rubber firmly bonded with the flat glass. The hardness of the silicone rubber part of the bonded composite was measured with a hardness meter for rubber to reveal that it was 5. Thus, the hardness was invariable. The bonded composite was subjected

to an adhesive joint failure test. A cohesive failure was observed in all the cases. For comparison, a cured silicone rubber was prepared in the same manner as above except that no vinyltrimethoxysilane was used. The comparative, cured silicone rubber peeled off from the surface of the flat glass and, therefore, no bonded composite could be obtained.

Example 2

10        95 parts of methyl(3,3,3-trifluoropropyl)-polysiloxane (a) having dimethylvinylsilyl groups at both ends thereof and a viscosity of 3,000 CS was mixed with 5 parts of methylhydrogenpolysiloxane having dimethyl(3,3,3-trifluoropropyl)silyl groups at both ends and a viscosity of 20 CS, 2 parts of hydrogentrimethoxysilane (f) [ $\text{HSi}(\text{OCH}_3)_3$ ], 5 ppm (in terms of platinum), based on the total amount, of vinylsiloxane complex salt of chloroplatinic acid (c) and 0.1 part of tetramethyltetravinylcyclotetrasiloxane (a). The value of [equivalents of silicon atom-bonded hydrogen atoms in component (b)] / [equivalents of silicon atom-bonded vinyl groups in component (a)] was 3/1. The mixture was poured into a polyethylene resin frame on a polyethylene film to a thickness of 6 mm and left to

stand in an open system in an oven filled with dry nitrogen at 100°C for 10 min to cure the same into a rubbery product. The cured silicone rubber was taken out of the oven and left to cool to room 5 temperature. The hardness of this product measured in the same manner as in Example 1 was 8. The cured silicone rubber was closely contacted with a surface of a copper or aluminum plate and left to stand in an oven at 50°C for 16 h and then taken 10 out to obtain a bonded composite comprising the cured silicone rubber firmly bonded with the copper or aluminum plate. The bonded composite was left to cool to room temperature and the hardness of the silicone rubber part thereof was measured. The 15 hardness was 8 in both cases. Thus, the hardness was invariable by this treatment. The bonded composite was subjected to an adhesive joint failure test. A cohesive failure was observed in both cases. For comparison, a cured silicone rubber 20 was prepared in the same manner as above except that no hydrogentrimethoxysilane was used. The comparative, cured silicone rubber peeled off from the surface in both cases and, therefore, excellent bonded composite could not be obtained.

25 Example 3

95 parts of dimethylsiloxane/methylphenylsiloxane copolymer (a) (molar ratio of the dimethylsiloxane units to the methylphenylsiloxane units = 90:10) having methylphenylvinylsilyl groups at both ends and a viscosity of 9,000 CS was mixed with 5 parts of dimethylsiloxane/methylhydrogensiloxane copolymer (b) (molar ratio of the dimethylsiloxane units to the methylhydrogensiloxane units = 50:50) having dimethylphenylsilyl groups at both ends and a viscosity of 20 CS, 4 parts of allyltrimethoxysilane (f), 5 ppm (in terms of platinum), based on the total weight, of vinylsiloxane complex salt of chloroplatinic acid (c) and 0.1 part of phenylbutynol. The mixture was poured into a tetrafluoroethylene resin frame placed on a tetrafluoroethylene resin film to a thickness of 3 mm. The surface of the poured mixture was covered with a tetrafluoroethylene resin film of a thickness of 10  $\mu\text{m}$  and then left to stand in an oven at 100°C for 10 min 10 to cure the same into a rubbery product. The cured product was taken out of the oven and left to cool to room temperature. The tetrafluoroethylene resin film and tetrafluoroethylene resin frame were removed and the hardness of the cured 15 silicone rubber was measured in the same manner 20 25

as in Example 1. The hardness was 5. The cured silicone rubber was interposed between two ceramic plates or between two epoxy resin FRP plates. They were pressed lightly, left to stand in an oven at 5 100°C for 60 min and taken out. Thus, a bonded composite comprising the cured silicone rubber interposed between the two epoxy resin FRP plates and firmly bonded with them was obtained.

10 The two plates constituting the resulting bonded composite were pulled in adverse directions from each other at an angle of 180°C. The silicone rubber part of the composite was broken. Namely, cohesive failure occurred.

Example 4

15 65 parts of dimethylpolysiloxane (a) having dimethylvinylsilyl groups at both ends and a viscosity of 2,000 CS was mixed with 35 parts of a copolymer (containing 2.5% of vinyl group) comprising  $\text{SiO}_2$  units,  $\text{Me}_3\text{SiO}_{0.5}$  units and  $\text{Me}_2\text{ViSiO}_{0.5}$  20 units in which Me represents a methyl group and Vi represents a vinyl group. 95 parts of the resulting mixture was mixed with 5 parts of methylhydrogenpolysiloxane (b) having trimethylsilyl groups at both ends and a viscosity of 30 CS, 2.0 25 parts of vinyltriacetoxy silane (f) and 5 ppm

(in terms of platinum), based on the total weight, of vinylsiloxane complex salt of chloroplatinic acid (c).. The value of [equivalents of silicon atom-bonded hydrogen atoms in component (b)] / [equivalents of silicon atom-bonded vinyl groups in component (a)] was 2/1. The mixture was laminated with a polypropylene film and a polyimide film in such a manner that the thickness of the silicone layer would be 0.10 mm. The laminate was cured by leaving it to stand in an oven at 100°C for 10 min. The laminate was taken out of the oven and left to cool to room temperature. The polypropylene film was peeled off. The cured silicone rubber bonded with the polyimide film was skived and its hardness was measured in the same manner as in Example 1. The hardness was 10. The silicone rubber part of the laminate comprising the cured silicone rubber and the polyimide film was closely contacted with a nickel plate and left to stand in an oven at 100°C for 30 min to obtain a bonded composite comprising the cured silicone rubber interposed between the polyimide film and the nickel plate and firmly bonded with them.

Example 5

25        80 parts of dimethylpolysiloxane (a) having

dimethylallylsilyl groups at both ends and a viscosity of 12,000 CS was mixed with 20 parts of fumed silica (specific surface area: 200 m<sup>2</sup>/g) the surface of which had been made hydrophobic by a treatment with trimethylsilyl groups by means of a kneader mixer. 95 parts of the resulting mixture was mixed with 5 parts of methylhydrogenpolysiloxane (b) having trimethylsilyl groups at both ends and a viscosity of 10 CS, 5 ppm (in terms of platinum), based on the total weight, of vinylsiloxane complex salt of chloroplatinic acid (c) and 1 part of vinyltris(methyl ethyl ketoxime)silane (f). The mixture was poured in a fluororesin mold to a thickness of 5 mm and then cured by leaving it in an oven filled with dry air in an open system at 150°C for 20 min to obtain a rubbery product. The product was taken out of the oven and left to cool to room temperature. The cured silicone rubber was taken out of the mold and its hardness was measured in the same manner as in Example 1. The hardness was 15. The cured silicone rubber was closely contacted with a glass plate and a ceramic plate and left to stand in an oven at 150°C for 60 min. The cured silicone rubber was firmly bonded with both plates. The hardness of the silicone rubber

part was measured again. The hardness was 15 and thus it was invariable. For comparison, a cured silicone rubber was prepared under the same conditions as above except that no vinyltris(methyl ethyl ketoxime)silane was used. This comparative product could not be bonded with the glass plate or ceramic plate.

5 Example 6

A cured silicone rubber and then a bonded composite thereof were prepared in the same manner as in Example 3 except that the allyltrimethoxysilane (f) was replaced with  $\gamma$ -methacryloxypropyltriethoxysilane (d) and the ceramic plate and the epoxy resin FRP plate were replaced with a quartz glass plate and an unsaturated polyester resin FRP plate, respectively. The hardness of the cured silicone rubber was 6. The cured silicone rubber was firmly bonded with the quartz glass plate and the unsaturated polyester resin FRP plate.

10 Example 7

A cured silicone rubber and then a bonded composite thereof were prepared in the same manner as in Example 5 except that the vinyltris(methyl ethyl ketoxime)silane (f) was replaced with diethoxydi(methyl ethyl ketoxime)silane (d) and

the glass plate was replaced with a steel plate. The hardness of the cured silicone rubber was 16. The cured silicone rubber was firmly bonded with the steel plate and the ceramic plate.

5      Example 8

A laminate comprising a silicone layer having a thickness of 1 mm and interposed between two polypropylene films was prepared in the same manner as in Example 4 except that the vinyltriacetoxy-silane (f) was replaced with a partial hydrolyzate of vinyltrimethoxysilane (f) (methoxy group content: 26%) and the polyimide film was replaced with a polypropylene film. The laminate was left to stand in an oven at 100°C for 10 min to effect the curing. 10  
The product was taken out of the oven and left to cool to room temperature. The two polypropylene films were peeled off and the hardness of the cured silicone rubber was measured in the same manner as in Example 1. The hardness was 8. The cured 15  
silicone was interposed between a glass plate and a copper plate and left to stand in an oven at 100°C for 30 min to obtain a bonded composite comprising the cured silicone rubber firmly bonded 20  
with the glass plate and the copper plate. 25

Example 9

93 parts of dimethylpolysiloxane (a) having dimethylvinylsilyl groups at both ends and a viscosity of 6,000 CS was mixed with 7 parts of methylhydrogensiloxane/methyl( $\gamma$ -trimethoxysilylpropyl)siloxane copolymer (b) [ratio of methylhydrogensiloxane units to methyl( $\gamma$ -trimethoxysilylpropyl)siloxane units = 20/10] having trimethylsilyl groups at both ends and a viscosity of 50 CS and 2 ppm (in terms of platinum), based on the total weight, of vinylsiloxane complex salt of chloroplatinic acid (c). A laminate was prepared from this mixture and a polyvinylidene fluoride film and a polypropylene film both surface-treated so as to improve the adhesion while the thickness of the silicone layer was controlled to 0.20 mm.

The laminate was left to stand in an oven at 100°C for 10 min to effect the curing. The product was taken out of the oven and left to cool to room temperature. The polypropylene film was peeled off.

The cured silicone bonded with the polyvinylidene fluoride film was closely contacted with a silicon wafer and left to stand in an oven at 100°C for 30 min to obtain a bonded composite comprising the cured silicone rubber interposed between the polyvinylidene fluoride film and the silicon wafer and

firmly bonded with them.

Example 10

97 parts of a dimethylsiloxane/methyl( $\beta$ -trimethoxysilyl-  
5 ethyl)siloxane copolymer (a) [ratio of  
dimethylsiloxane units to methyl( $\beta$ -trimethoxysilyl-  
ethyl)siloxane units = 95/5] having dimethylvinyl  
groups at both ends and a viscosity of 500 CS was  
mixed with 3 parts of methylhydrogensiloxane (b)  
having trimethylsilyl groups at both ends and a  
10 viscosity of 20 CS and 3 ppm (in terms of platinum),  
based on the total weight, of vinylsiloxane complex  
salt of chloroplatinic acid (c). A glass cloth was  
impregnated with the mixture to a thickness of 1 mm  
to form a coating. Polypropylene films were applied  
15 to both surfaces of the coated cloth to form a  
laminate. The laminate was left to stand in an oven  
at 100°C for 10 min to cure the same. The laminate  
was taken out of the oven and left to cool to room  
temperature. The polypropylene films were removed  
20 by peeling from both surfaces of the coated glass  
cloth. The glass cloth was closely contacted with  
an aluminum foil having a thickness of 0.5 mm and  
left to stand in an oven at 190°C for 15 min to  
obtain a composite comprising the cured silicone  
25 rubber firmly bonded with the aluminum foil.

Example 11

97 parts of dimethylpolysiloxane (a) having dimethylvinylsilyl groups at both ends and a viscosity of 2,000 CS was mixed with 3 parts of methylhydrogenpolysiloxane (b) having trimethylsilyl groups at both ends and 2 ppm (in terms of platinum), based on the total weight, of vinylsiloxane complex salt of chloroplatinic acid (c).  
5 The mixture was poured into a mold having a thickness of 1 mm and left to stand in an oven at 100°C for 20 min to obtain a cured silicone rubber sheet.  
10 The sheet was cooled to room temperature. Ethyl polysilicate (e) (silicon atom-bonded ethoxy group content: 0.2%) was applied to the surface of the  
15 sheet and the sheet was left to stand at room temperature for 10 min. The ethyl silicate-coated surface of the sheet was closely contacted with the surface of a glass and left to stand in an oven at 100°C for 30 min to obtain a composite comprising a firmly bonded silicone rubber sheet and glass.  
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Industrial Applicability:

According to the process of the present invention, a bonded composite of a cured product of an addition reaction-curable silicone and a solid substance can be produced easily and surely with  
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a high precision. Therefore, according to the process of the invention, qualities of various products coated with a cured silicone can be improved and the uses of them can be broadened.

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WHAT IS CLAIMED IS:

1. A process for producing a bonded composite of a cured silicone and a solid substance characterized in that a cured product of an addition reaction-curable silicone containing 0.05 to 20 wt.% of a silicon atom-bonded hydrolyzable group is kept in contact with the solid substance at room temperature or a higher temperature.  
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2. A process according to Claim 1 wherein said silicon atom-bonded hydrolyzable group is contained in an organosilicon compound contained in free form in said cured product of an addition reaction-curable silicone.  
10
3. A process according to Claim 1 wherein said silicon atom-bonded hydrolyzable group is contained in a polysiloxane constituting said cured product of an addition reaction-curable silicone.  
15
4. A process according to Claim 1 wherein said cured silicone is a rubbery substance having a hardness of up to 20.  
20
5. A process according to Claim 1 wherein said room temperature or higher temperature ranges from 40 to 200°C.
6. A process according to Claim 1 wherein said cured silicone is a laminate thereof with another  
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material having no releasing property.

7. A process according to Claim 6 wherein said another material is in the form of a heat-resistant sheet or film.

5       8. A process according to Claim 7 wherein said cured silicone is in the form of a sheet or film and one surface of the sheet or film is laminated with a heat-resistant sheet or film having no releasing property.

10      9. A process according to Claim 8 wherein said cured silicone is in the form of a sheet or film, one surface of which is laminated with a heat-resistant sheet or film having no releasing property and the other surface of which is coated with a releasing sheet or film, and the laminate is bonded with a solid substance after the releasing sheet or film has been peeled off.

15      10. A process according to Claim 1 wherein said cured silicone is in the form of a sheet or film one or both surfaces of which is(are) coated with a releasing sheet or film, and said cured silicone is contacted with a solid substance after at least one of said releasing sheet(s) or film(s) has(have) been peeled off.

## INTERNATIONAL SEARCH REPORT

0136358

International Application No. PCT/JP84/00041

## I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl<sup>3</sup> B29H 9/10, B32B 25/10, B32B 27/00

## II. FIELDS SEARCHED

## Minimum Documentation Searched \*

Classification System	Classification Symbols
IPC	B29H 9/10, B32B 25/10, B32B 27/00, C08L 83/04, C08K 5/54, C09J 3/16
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *	

## III. DOCUMENTS CONSIDERED TO BE RELEVANT \*\*

Category*	Citation of Document, ** with indication, where appropriate, of the relevant passages ***	Relevant to Claim No. ***
X	JP, B2, 56-9183 (Shin-Etsu Chemical Co., Ltd.) 27 February 1981 (27. 02. 81) & US, A, 4,196,273	1 - 10
X	JP, B2, 57-5836 (Toshiba Silicone Co., Ltd.) 2 February 1982 (02. 02. 82)	1 - 10
Y	JP, A, 51-139854 (Toshiba Silicone Co., Ltd.) 2 December 1976 (02. 12. 76)	1 - 10
A	JP, A, 54-48853 (Toshiba Silicone Co., Ltd.) 17 April 1979 (17. 04. 79) & US, A, 4,257,936	1 - 10
A	JP, B2, 52-48146 (Toray Silicone Co., Ltd.) 7 December 1977 (07. 12. 77) & DE, A, 2,636,185 & FR, A, 2,321,523 & US, A, 1,664,676 & GB, A, 1,561,763	1 - 10
A	JP, B2, 55-41702 (Shin-Etsu Chemical Co., Ltd.) 25 October 1980 (25. 10. 80)	1 - 10

\* Special categories of cited documents: \*\*

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search \*

April 25, 1984 (25. 04. 84)

Date of Mailing of this International Search Report \*

May 14, 1984 (14. 05. 84)

International Searching Authority \*

Japanese Patent Office

Signature of Authorized Officer \*\*

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	JP, B2, 55-21782 (Dow Corning Corp.) 12 June 1980 (12. 06. 80) & US, A, 4,087,585 & DE, A, 2,809,588 & GB, A, 1,577,511	1 - 10
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V.  OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE<sup>12</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.  Claim numbers ..... because they relate to subject matter<sup>13</sup> not required to be searched by this Authority, namely:

2.  Claim numbers ..... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out<sup>14</sup>, specifically:

VI.  OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING<sup>15</sup>

This International Searching Authority found multiple inventions in this international application as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4.  As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.

